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"Four-letters" ($\gamma \rightarrow \varepsilon \rightarrow \beta \rightarrow \alpha$) thermal transformation of Si-rich ferrihydrite

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Ferrihydrite is a poorly ordered iron (oxyhydr)oxide, ubiquitous in near-surface environments, where it is an important scavenger of numerous toxic metals and metalloids (Cornell & Schwertmann 2003). Being metastable, ferrihydrite transforms with time into stable phases, usually goethite and/or hematite. The latter is also a final product of ferrihydrite thermal conversion via both, hydrothermal and dry-heating pathways. The transformation course is affected by many factors and for this reason its details are still under debate. Pure ferrihydrite practically does not exist in nature. The admixtures present in its composition affect many properties of the oxyhydroxide, including surface chemistry, sorption effectiveness, crystallinity, magnetic ordering and solubility. Silicate, probably the most important natural impurity, was shown to hamper thermal transformation of ferrihydrite. The process was studied in detail only for relatively low-Si samples (Campbell et al. 2002). In some environments, such as modern seafloor hydrothermal vents, higher Si/Fe proportion have been found (Sun et al. 2013). The objective of this work was to determine if (and if so, how) the high silicate content in ferrihydrite modifies its thermal transformation.

Ferrihydrite samples of high Si/Fe molar ratios (0.50, 0.75, 1.00, and 1.50) were obtained by reaction of $Fe_2(SO_4)_3$ with NaOH in the presence of Na_2SiO_3 at pH 8.2 (Vempati & Loeppert 1989). The products were characterized using X-ray powder diffractometry (XRD), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, and scanning electron microscopy (SEM). Simultaneous thermal analyses, including differential thermal analysis (DTA), thermogravimetry (TG) and quadrupole mass spectrometry of evolved gases (QMS) were also performed. All of the ferrihydrites were heated from 30°C · min^{-1} to 1000°C · min^{-1}, at 10°C · min^{-1} in flowing air, using preheated sample as an inert material. The samples were also heated to various temperatures, chosen on the basis of the analysis of their thermal patterns. The heating was stopped immediately when reaching the desired temperature. The sample was removed, rapidly cooled in air and characterized again by XRD, FTIR and SEM.

The thermal patterns revealed that the presence of Si in ferrihydrite hampers its conversion to hematite, which is reflected by shifting of the hematite crystallization exotherm to temperature as high as ca. 920°C, in comparison to 350–460°C when Si-free ferrihydrite is annealed (Pieczara et al. 2014). XRD patterns and FTIR spectra of the samples heated to 1000°C show the presence of hematite and cristobalite. It was observed that the higher molar Si-to-Fe ratio in initial mineral results in the higher cristobalite concentration in the product. SEM observation showed that hematite crystallites, embedded in cryptocrystalline silica, are distinctly smaller than those produced from pure ferrihydrite. They also exhibit wider range of crystal habits – isometric grains, plates, rods and even needles were encountered. Elongated crystallites (rods and needles) appear to be more common in the highest-Si products.

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Moreover, whilst during transformation of pure ferrihydrite into hematite no distinct intermediate phase is formed, the conversion of high-Si ferrihydrite proceeds by much more complex pathway. After low-temperature dehydration, the material still exhibits two-peak ferrihydrite-like XRD pattern, but a gradual amorphisation is observed up to ca. 600°C. Then, at 650°C amorphous silica emerges which is followed by the formation of nanocrystalline maghemite (γ-Fe_2O_3) between 700°C and 800°C. Subsequently, maghemite is transformed to orthorhombic ε-Fe_2O_3 phase at 800–850°C. In the samples of 0.50, 0.75 and 1.0 Si/Fe ratios, further increase of temperature results in ε-Fe_2O_3 conversion to hematite and crystallization of cristobalite-like phase. However, XRD patterns of annealed the highest-Si sample (Si/Fe = 1.5) show also the presence of β-Fe_2O_3 between 907°C and 930°C. At 907°C hematite appears and ε-Fe_2O_3 vanishes by 930°C, so at the latter temperature two Fe_2O_3 polymorphs (α and β) are present. At 1000°C hematite is the sole iron oxide in all the products. Thus siliceous ferrihydrites transform into hematite via γ–ε or γ–ε–β pathway, depending on the Si/Fe ratio. Formation of rare epsilon and beta iron oxide polymorphs from high-Si ferrihydrites can be explained by emerging of amorphous SiO_2 during annealing, which subsequently acts as anti-sintering agent stabilizing maghemite precursor against its direct thermal conversion to hematite.

Our results show that high silicate content causes not only the retarding of ferrihydrite conversion to hematite but also affects crystallinity of the product and complicates the transformation pathway. In the authors' opinion the formation of rare epsilon and beta Fe_2O_3 is noteworthy for at least two reasons. Firstly, β- and, especially, ε-Fe_2O_3 have been recently found to exhibit many interesting physical properties, which make them attractive nanomaterials for use in a wide range of applications (Machala et al. 2011). Annealing of Si-ferrihydrites might offer an alternative method of obtaining these oxides. Secondly, both these oxides have not been found in nature yet. This work suggests that their formation is possible in places where siliceous ferrihydrites or other Si-Fe amorphous sediments have been heated to high temperature, as in e.g. hydrothermal systems of mid-ocean ridges.

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